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<b>(54) Title:</b> PACKAGING MATERIAL HAVING IMPROVED BARRIER PROPERTIES  <b>(57) Abstract</b>  A composite material suitable for packaging moisture or oxygen sensitive products comprising one or more polymeric substrate(s) and one or more barrier property-providing coating(s), ink(s) and/or adhesive(s) on or between said substrate(s) being cured from composition(s) comprising alpha, beta ethylenically unsaturated monomer(s) and/or oligomer(s). A method for providing barrier properties to a polymeric substrate comprising applying a barrier property-providing amount of a composition comprising alpha, beta ethylenically unsaturated monomer(s) and/or oligomer(s) as a coating, ink or adhesive on the substrate or between two or more of said substrates; and curing the composition. Articles comprising perishable material or articles enclosed within a package comprised of such composite material.		

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## PACKAGING MATERIAL HAVING IMPROVED BARRIER PROPERTIES.

This invention relates to the field of packaging materials which are designed to resist moisture, vapor and oxygen transmission.

Packaging materials designed to resist moisture, vapor and oxygen transmission are used to package a wide variety of materials and articles, for example, foods, metals, electronic articles and medical devices.

Typical packaging materials for moisture and oxygen sensitive materials and articles are laminates which include polymeric substrates. The polymeric substrates are most frequently polyolefins such as polypropylene, polyethylene, and the like. While such substrates do not have barrier properties on their own, barrier properties are frequently obtained by metallizing one or more of such polymeric film substrates, and/or by including a barrier substrate of polyethylene terephthalate (PET), polycarbonate, or polyvinylidene chloride. Such composite packaging materials may be either clear or opaque and may include a printed layer comprised of ink. When a metallized polymeric substrate layer is included, the metallization is typically from sputtered aluminium. Metallization has been found to be necessary in many cases in order to obtain suitable barrier properties. Metallization has been used frequently with polypropylene and PET film to impart moisture vapor transmission and oxygen transmission barrier properties. Packaging materials used for perishable materials and articles are typically composites which comprise one or more substrates which are laminated together. The polymeric substrates can be of varying thicknesses, from that of thin films to much thicker materials such as the polyethylene terephthalate blow molded materials used for carbonated beverage bottles.

As an example of a packaging composite, a typical orange juice carton is comprised of (in order of layers starting from the food contact layer) a 1 mm polypropylene film substrate ; a water or solvent based adhesive ; paper board ; another layer of adhesive ; metallized PET as the moisture barrier ; adhesive ; polypropylene or paper ; printing with conventional water based inks ; and an electron beam cured coating to protect against abrasion and provide gloss.

As another example, a potato chip bag is typically a 1 mm to 1.4 mm polypropylene film substrate, a solvent or water based

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adhesive ; metallized PET as a barrier layer ; conventional water or solvent based ink ; and a polypropylene layer to protect the ink. There are no radiation cured layers in this typical food bag.

A typical packaging material for electronic components  
5 such circuit boards would have a 1.5 mil (0.0381 mm) metallized polypropylene barrier film, a conventional solvent-based adhesive, polypropylene or PET film, and then conventional solvent or water based printing.

Cornforth et al., U.S. Patent 5,418,016, disclose a coating  
10 process using radiation curable compositions which include N-vinylformamide rather than conventional acrylic monomers. Cornforth et al. disclose that the N-vinylformamide exhibits superior capacity to reduce the working viscosity of the oligomer, and is especially useful with polyurethane (meth)acrylate-containing formulations with which  
15 viscosity reduction is particularly difficult with monomers traditionally used with such systems, and that films cured with N-vinylformamide demonstrate excellent hardness, chemical resistance, flexibility, scuff resistance and scratch resistance. Cornforth et al. do not disclose use of the coated films in packaging materials, nor do they disclose the  
20 coatings as providing barrier properties.

Costin et al., U.S. Pat. 5,656,703, disclose radiation curable coating compositions containing an epoxy resin and a poly(meth)acrylate, including a metal di(meth)acrylate adhesion promoting agent and a polyamine curing agent. This patent does not  
25 address barrier properties of packaging materials comprising polymeric film substrates.

U.S. Pat. 4,156,035, assigned to W.R. Grace, disclosed photopolymerizable compositions comprising mixtures of (meth)acrylate-terminated monomers and epoxy resin compositions  
30 which can be cured by exposure to radiant energy (i.e., radiation) and methods therefor. According to this patent, mixtures of epoxy resins with acrylic or methacrylic monomers can be photocured in air by Group VIa onium salts, in particular sulfonium salts, in combination with free radical photoinitiators such as benzoin ethers, in thick  
35 sections tack-free and, hence, these formulations show neither the disadvantages of the photocurable epoxy systems nor the photocurable acrylics when cured separately, and can be used as coatings that can

be UV cured in air on a wide variety of substrates such as paper, wood, glass, aluminium, tin plate, and plastic. These systems, known as "hybrid" radiation curable systems, have not been recognized as providing barrier properties, nor have they been used as coatings, inks, or adhesives in packaging composite materials.

Crivello, U.S. Pats. 5,567,858 ; 5,260,349 and 4,069,055, disclosed propenyl ether monomers which are readily polymerized in the presence of cationic photoinitiators, when exposed to actinic radiation, to form poly(propenyl ethers) that are useful for coatings, sealants, varnishes and adhesives, but such "cationic" radiation curable systems have not been recognized as suitable for providing barrier properties to packaging composites.

U.S. Pat. 5,446,073 to Jonsson et al., assigned to Fusion Systems Corporation, disclosed charge transfer radiation curable compositions containing a charge transfer complex from at least one unsaturated compound having an electron donor group and having an electron withdrawing group and being free of any photoinitiating compound, polymerized by being subjected to ultraviolet light. For example, charge transfer complex from a 1:1 ratio of double bonds of maleic anhydride and ethylene glycol divinyl ether formed a hard, fully cured coating throughout the thickness of the coating. These types of radiation curable polymerization systems are known as "charge transfer" systems. They have not heretofore been recognized as providing barrier properties to packaging composite materials.

U.S. Pat. 4,201,642, assigned to Celanese Corp., discloses a radiation curable resin composition comprising a blend of 10-30 wt.% chlorinated rubber, 2-25% chlorinated paraffin, 15-45% vinyl alkanoate, 10-40 wt.% crosslinking monomer containing more than 2 polymerizable double bonds, and 0.5-15 wt.% photoinitiator, used as a moisture barrier film for protecting paper or cardboard. This patent does not teach protecting moisture or oxygen sensitive products with moisture vapor and oxygen transmission-resistant packaging. Furthermore, compositions comprising 10-30 wt.% chlorinated rubber and 2-25% chlorinated paraffin are not within the scope of the present invention.

U.S. Pat. 4,230,550, assigned to Hewlett Packard, discloses a solvent resistant radiation curable barrier coating based on

a polyfunctional melamine compound. This patent does not teach moisture vapor or oxygen transmission resistance.

European Patent 77061-A2, assigned to Dow Corning Corp, and E.P. 0832945-A2, assigned to Dow Corning Torah Company Ltd, disclose a radiation curable silicone composition having abrasion resistance and barrier properties. The present invention avoids the use of the amino group-containing silanes required by this reference.

Mitsubishi Paper Mills Ltd., JP 06033394-A discloses release paper for sticking labels having a barrier layer consisting of silicone resin, which is excluded from the present invention.

Williams et al. (Avery Dennison Corp.), U.S. Pat. 5,436,073, disclose a composite laminate for pressure sensitive adhesive sheets comprising a paper substrate coated with radiation-cured acrylic composition and a polyolefin film, useful for release sheets and pressure-sensitive adhesive sheets, e.g. for the food industry. This patent does not teach moisture paper and oxygen transmission resistance, nor suitability for packaging moisture or oxygen sensitive products.

Kuraray Co. Lt., JP 09157421-A discloses wrapping materials for retort food having a coating comprising vinyl alcohol type resins, which are excluded from the present invention.

Standard Oil Co. (Ohio) Australian published application AU 8666600-A discloses a coating composition comprising a nitrile monomer, acrylate monomer, and reactive diluent, but does not disclose suitability to package moisture paper or oxygen sensitive products.

Yoshiro Kogyosho KK Japanese Patent J57038-828 (Derwent Abstract 29428 E/15) discloses a polyester bottle having gas barrier properties coated with a UV cured resin composition formed from unsaturated polyester, acrylic, alkyd, epoxy, urethane resin, modified resin or copolymer. The coating is not disclosed as having barrier properties. J59014-949 A is similar to this patent.

Eastman Kodak U.S. Pat. 4,070,398 discloses packaging moisture or oxygen sensitive products with metal foil laminated with radiation curable layers. It teaches metal foil providing oxygen and moisture barrier properties to a composite material used for packaging. The foil is coated with chemical resistance-providing

coating compositions. The present invention achieves barrier properties without the metal foil.

Sharp, WO 97/34959, discloses a release liner for a substrate for use in pressure-sensitive adhesive applications having a radiation curable barrier layer for use between the substrate and the silicon layer. The barrier layer is not disclosed to provide moisture and vapor transmission resistance for composites used as packaging materials.

Curatolo (Avery Dennison Corp.) WO 97/25389 discloses a radiation-curable coating composition comprising about 70-90 wt.% polyfunctional acrylate monomer, about 1-30 wt.% other vinyl or unsaturated monomer used to be deposited on polymeric film to improve printability and other surface characteristics. This publication does not disclose moisture vapor and oxygen barrier properties being improved by the coating.

Lucas (International Paper Co.) U.S. Pat. 5,340,620 discloses solvent or water based coating compositions which must be dried, used for paper board but not disclosed for moisture or oxygen sensitive product packaging. Alkoxyamino silanes are required, but are excluded from the present invention.

It has been a long felt need to improve the barrier properties of packaging materials which are comprised of one or more polymeric substrates. In the case of packaging materials comprising a metallized film substrate, there has been a long felt need to either eliminate the metallization step without reducing barrier properties, or to improve the barrier properties without eliminating the metallization step or the metallized film substrate.

Radiation curing, especially by ultraviolet (UV) light or electron beam (EB), of 100% solid systems is desirable for a number of reasons including high efficiency, high productivity and improved environmental acceptability. With 100% solid systems cured by UV or EB technology, no solvents are required, and this results in reduced pollution possibilities as well as reduced capital equipment and process costs due to the lack of solvent evaporation and recovery requirements. In addition, the absence of a solvent results in higher line speeds without the limitations of oven-drying capabilities, and curing occurs rapidly at low temperatures which reduces process

effects on substrates which may be heat-sensitive. The coatings themselves generally have fewer defects and, consequently, improved properties since it is not necessary for solvent molecules to diffuse out of the coating during cure. For the reasons outlined above, space requirements, waste, and energy consumption are also lower with radiation-curable systems.

Radiation curing of polymeric systems may utilize electron beam curing or ultraviolet curing. UV curing of polymeric systems requires the presence of at least one photoinitiator whereas curing by EB techniques does not require a photoinitiator. With the exception of the presence or absence of photoinitiator, the formulations cured by either UV or EB technology may otherwise be identical.

The present invention which provides a solution to these long felt needs comprises in one aspect a composite packaging material comprising one or more polymeric substrates and one or more barrier-providing coating(s), ink(s) and/or adhesive(s) cured from compositions comprising alpha, beta ethylenically unsaturated monomer(s) and/or oligomer(s). The composite does not comprise metal foil, and the compositions do not comprise amino group-containing alkoxy silane compounds or vinyl alcohol resins.

In another aspect, the invention comprises a method of improving the barrier properties of a packaging material comprising applying such a coating, ink, or adhesive composition to the substrate(s) and curing.

Another aspect of the invention is a package of perishable material or article, which comprises such composite packaging material.

The packaging material of the invention is generally comprised of one or more polymeric substrates which can be paper, cardboard, polymeric film or any combination thereof. The packaging material can vary widely in thickness depending on the application. Usually, the thickness of each of the polymeric film substrates is about 10 to 200 microns, and the composite material is comprised of at least two of the polymeric films, having adhesive between each film substrate. Paper and cardboard substrates can be thicker than 200 microns, depending on the application. Applications such as food, metals, electronics and medical device packaging require a wide variety



of packaging materials. The packaging materials can be clear or opaque, can comprise a pigment, and can be in the form of an ink which is used to print a design on the packaging. The common feature of the packaging materials used in this invention is that they provide  
5 barrier properties to moisture vapor, oxygen and/or carbon dioxide. The packaging materials protect food or other items from oxidation or spoiling due to moisture. In some cases, the materials are designed to contain gas such as carbonation. The polymeric film substrate can be any type of polymer used in the art of packaging materials, e.g.,  
10 polyvinylidene chloride, polyethylene, polypropylene, polyamide, cellulosic, polystyrene, poly(meth)acrylate, and poly(ethylene terephthalate). When the film is metallized, it can be metallized with any known method, for example using sputtered aluminium according to conventional processes.

15 A wide variety of compositions can be used for the coating, ink or adhesives used in the invention to provide barrier properties. In general, the curable compositions comprise alpha, beta ethylenically unsaturated monomer(s) and/or oligomer(s). The compositions are curable either through a free radical mechanism, as is the case for  
20 (meth)acrylate monomers and oligomers, for example, or through cationic, charge transfer, or hybrid mechanisms. Throughout this specification and claims, the terms "(meth)acrylic" and "(meth)acrylate" are used generally to include derivatives of acrylic acids as well as methacrylic acids, including the esters. The term "methacrylate" is  
25 used to include of methacrylic esters.

Examples of hybrid mechanisms, generally comprising mixtures of (meth)acrylate-terminated monomers and epoxy resin, are set forth in the aforementioned U.S. Pat. 4,156,035, which is incorporated herein by reference.

30 Examples of charge transfer mechanisms are set forth in the aforementioned U.S. Pat. 5,446,073, which is also incorporated by reference.

Examples of cationic mechanisms are set forth in the aforementioned Crivello Patents, 5,567,858 ; 5,260,349 ; and  
35 4,069,055, which are incorporated by reference. Especially preferred cationic systems include propenyl ether monomers.

In the case of cationic, hybrid and charge transfer systems, the curing is conducted with radiation. In the case of free radical systems, the curing is preferably, but not necessarily, conducted with radiation.

5 Free radical systems are preferably (meth)acrylate based, i.e., comprise either (meth)acrylate oligomers, monomers, or, preferably, both.

The free radical curable oligomers preferably fall into at least eight broad groups : polyether acrylates, epoxy-acrylates, 10 polyester acrylates and polyurethane acrylates, (meth)acrylated acrylic oligomers, fluorinated (meth)acrylated acrylic oligomers, polyamine acrylates and "long chain" C<sub>4</sub>-C<sub>18</sub> alkane diol methacrylates. Polyether acrylates are the reaction product between (meth)acrylic acid and polyether polyols. Preferable polyether acrylates are polyethylene 15 glycol or polypropylene glycol di(meth)acrylates, or di(meth)acrylates of mixed ethoxy/propoxy-based polyether diols. The epoxy-acrylates include the  $\beta$ -hydroxy esters which are generated by the reaction of acrylic acid or methacrylic acid with an epoxy resin or epoxy-novolak resin. The polyester acrylates consist of polyesters which have been 20 esterified with (meth)acrylic acid to yield a polyester with acrylate ester terminal groups, using well established esterification techniques. The polyurethane acrylates consist of reaction products of a hydroxy-containing acrylate ester, usually 2-hydroxyethyl acrylate or hydroxy propyl acrylate with an isocyanate prepolymer. (Meth)acrylated acrylic 25 oligomers are obtained from oligomeric copolymers of at least one (meth)acrylic ester of C<sub>1</sub>-C<sub>18</sub> alcohols with (meth)acrylic acid and then at least a partial esterification of the carboxy groups by a methacrylic epoxide, like glycidyl methacrylate or epoxidized DCPD (meth)acrylate or from oligomeric copolymers of a (meth)acrylic ester of C<sub>1</sub>-C<sub>18</sub> 30 alcohols with a methacrylic epoxide, like glycidyl methacrylate or DCPD (meth)acrylate and then at least a partial esterification by (meth)acrylic acid. Fluorinated equivalent oligomers are obtained from fluorinated (meth)acrylates. Polyamine acrylates are essentially Michael reaction adducts between a multifunctional (meth)acrylate 35 and an amine or polyamine. Preferred oligomers are aliphatic polyether urethane (meth)acrylates ; aliphatic polyester urethane (meth)acrylates ; aromatic polyether urethane (meth)acrylates ;

aromatic polyester urethane (meth)acrylates ; polyester (meth)acrylates ; polyether (meth)acrylates ; epoxy (meth)acrylates ; polyamine (meth)acrylates ; and (meth)acrylated acrylic oligomers. Examples of suitable oligomers useful in the radiation-curable compositions of the invention include the following types of (meth)acrylates : aliphatic polyether urethane (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; aliphatic polyester urethane (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; aromatic polyether urethane (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; aromatic polyester urethane (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; polyether (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; epoxy (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; polyamine (meth)acrylates, di(meth)acrylates and poly(meth)acrylates ; (meth)acrylated acrylic oligomers ; and long chain alkane (meth)acrylates. Suitable "long chain" (meth)acrylates include, for example, 1,4-butane diol diacrylate, 1,5-pentane diol diacrylate, 1,6-hexane diol diacrylate, 1,8-octane diol diacrylate, 1,10-decane diol diacrylate, 1,12-dodecane diol diacrylate, and the like. Such long chain alkane (meth)acrylates can also be considered to be monomers. Other (meth)acrylated oligomers may be (meth)acrylated styrene-maleic anhydride or styrene-(meth)acrylic acid copolymers or (meth)acrylated derivatives of hydroxy-containing polybutadiene or polyisobutene oligomers, comprising ester or urethane groups. Acrylates are generally preferred over the corresponding methacrylates because of higher cure speed.

The oligomers are usually blended with a monomer in order to produce a radiation curable formulation of the appropriate viscosity for any particular application. The ratio by weight of oligomers to monomers can be from 0:100 to 100:0, and preferably about 50:50 to 95:5, more preferably about 80:20 to 90:10, and most preferably about 85:15.

Preferably, monomers are blended with the oligomers in order to yield a practical radiation curable formulation. Such monomers fall into three groups defined by functionality, and may be mono-, di- or poly-functional. Poly-functional monomers, usually with a functionality of 3 or 4, generally consist of (meth)acrylate esters of tri

or tetra-functional alcohols. Commonly used materials include glycerol triacrylate, trimethylol propane triacrylate, trimethylol ethane triacrylate, pentaerythritol tetraacrylate, together with the acrylates of the ethoxylates or propoxylates of the above alcohols. Di-functional monomers consist usually of the acrylate esters of ethylene glycol or propylene glycol, with tripropylene glycol diacrylate being especially preferred, diacrylates of longer chain alcohols such as hexanediol diacrylate and acrylate esters of cycloaliphatic diols such as the cyclohexane diols. Mono functional monomers consist of the acrylate esters of mono functional alcohols such as octanol, nonanol, decanol, dodecanol, tri decanol and hexadecanol both in their linear and branch chain forms. Also included are cyclohexyl acrylate and its alkyl derivatives such as t-butyl cyclohexyl acrylate, tetrahydro furfuryl acrylate. Specific examples of mono- and polyfunctional monomers which can be utilized as a reactive material in the coating compositions of the present invention include one or more of the following : ethylhexyl acrylate; 2-ethoxyethyl acrylate ; cyclohexyl acrylate ; lauryl acrylate ; stearyl acrylate ; alkoxyated phenol acrylates ; alkoxyated nonylphenol acrylates ; nonylphenol acrylate ; isobornyl acrylate ; acrylated epoxy soya oil ; acrylated epoxy linseed oil ; caprolactone acrylate ; 2-phenoxyethyl acrylate ; benzyl acrylate ; monomethoxy tripropylene glycol monoacrylate ; monomethoxy neopentyl glycol propoxylate monoacrylate ; 1,3-propanediol diacrylate ; 1,4-butanediol diacrylate ; 1,6-hexanediol diacrylate ; trimethylolpropane triacrylate ; glyceryl triacrylate ; pentaerythritol triacrylate ; pentaerythritoltetraacrylate ; dipentaerythritol pentaacrylate ; di-trimethylolpropane tetraacrylate ; tris(2-hydroxyethyl)isocyanurate triacrylate ; tetrahydrofurfuryl acrylate ; isooctyl acrylate ; isodecyl acrylate ; 2-(2-ethoxyethoxy) ethyl acrylate ; ethylene glycol diacrylate ; propylene glycol diacrylate ; neopentyl glycol diacrylate ; cyclopentenyl oxyethyl acrylate ; 9-anthracenyl methyl acrylate ; 1-pyrenylmethyl acrylate ; Fluorescein diacrylate ; and 3,8-diacryloyl ethidium bromide.

Specific examples of suitable polyfunctional (meth)acrylate monomers include the following (meth)acrylate compounds : diethylene glycol di(meth)acrylate ; triethylene glycol di(meth)acrylate ; tetraethylene glycol di(meth)acrylate ; dipropylene glycol

di(meth)acrylate ; tripropylene glycol di(meth)acrylate ; tetrapropylene glycol di(meth)acrylate ; glyceryl ethoxylate di(meth)acrylate ; glyceryl propoxylate di(meth)acrylate ; glyceryl ethoxylate tri(meth)acrylate ; glyceryl propoxylate tri(meth)acrylate ; trimethylolpropane ethoxylate tri(meth)acrylate ; trimethylolpropane propoxylate tri(meth)acrylate ;  
5 neopentylglycol ethoxylate di(meth)acrylate ; neopentylglycol propoxylate di(meth)acrylate ; monomethoxy trimethylolpropane ethoxylate di(meth)acrylate ; pentaerythritol ethoxylate tetra(meth)acrylate ; pentaerythritol propoxylate tetra(meth)acrylate ;  
10 dipentaerythritol ethoxylate penta(meth)acrylate ; dipentaerythritol propoxylate penta(meth)acrylate ; di-trimethylolpropane ethoxylate tetra(meth)acrylate ; Bisphenol A ethoxylate di(meth)acrylate ; Bisphenol A propoxylate di(meth)acrylate ; 1,8-octanediol di(meth)acrylate ; 1,10-decanediol di(meth)acrylate ; polybutadiene  
15 di(meth)acrylate.

Generally, (meth)acrylate monomers with higher molecular weights are preferred due to lower volatility and lower odor. As the molecular weight is increased, however, there is generally an increase in viscosity so that the upper limit of molecular weight for monomers  
20 and oligomers may be determined based on viscosity considerations. A low overall viscosity generally is desired for fast wetout and coating at high speeds. The oligomers useful in the present invention have calculated molecular weights preferably from about 150 to about 15,000, more preferably about 300 to about 5,000 or 10,000, and most  
25 preferably from about 300 to about 3,000. The molecular weight is either a calculated molecular weight based on the sum of the atomic weights of the atoms making up the oligomer, or the molecular weight is a number average molecular weight ( $M_n$ ) which may be determined by end group analysis.

30 The polymerization of the coatings, ink, and/or adhesives can be by any known method(s), for example, by oxidation, cross linking via electrons from an electron accelerator (electron beam or EB), peroxide decomposition which produces free radicals, ultraviolet light induced free radicals (UV curing), or a combination of these  
35 mechanisms. EB and UV are the preferred methods of curing, with EB being the most preferred. The preferred curing system is the use of UV and/or EB supplied by EB accelerators or gamma rays from uranium

or cobalt 60 or plutonium fission and typically the curing is done on a continuous line of film transported at speeds to 1-2,000 feet per minute. A photoinitiator may optionally be added to the oligomer composition prior to applying the composition to the polymeric film.

5 The oligomer-containing composition can be clear or pigmented, and can contain coloring materials, whether in the form of a coating, ink, or adhesive. When such composition is in the form of an adhesive, it is formulated according to known procedures and can be applied on one substrate prior to applying the next substrate on the adhesive, or  
10 it can be applied between two substrates continuously, prior to application of pressure to bond the adhesive between the two substrates, followed by curing. The preferred curing method for adhesives is radiation, which is different than that typically used in this art. The thickness of the coating(s), ink(s), and/or adhesive(s) is  
15 preferably about 1 to 250 microns. In most cases, the thickness is about 2 to 10 microns.

Typical packaging composites are comprised of one or more such substrates and from one to about twenty layers of coating, adhesive or ink. The most typical number of coatings, adhesives or  
20 inks is one to about three. The substrates are optionally metallized directly on the surface or first primed and then metallized and then coated, laminated, printed with ink, pressure sensitive adhesive or hot melt, or may be hot stamped to give a single layer or multi-layered construction of up to fifty layers. The layers could be combinations of  
25 any of the substrate materials and adhesives, coatings or printing ink materials. One typical composite comprises at least one polypropylene film substrate, at least one polyethylene terephthalate film substrate, and at least one radiation cured, barrier property-providing adhesive between said film substrates, wherein the adhesive is polymerized from  
30 a composition comprising a mixture of a (meth)acrylic functional oligomer and a (meth)acrylic functional monomer.

Moisture vapor transmission rates (MVTR) reflect the ability of food packaging to preserve the freshness or crispness of food when enclosed in flexible packaging, and the ability of other forms of  
35 composite materials used in packaging to prevent moisture from affecting the material or article which is encased by the package made of the composite material. MVTR is measured as the number of grams

of moisture that will pass through a one square meter sheet of film in a single day at 37.8°C (100F) and 90% relative humidity. The MVTR's achieved by the invention are generally less than 7.6 g/m<sup>2</sup> day. In preferred embodiments, MVTR's of less than 3.87 g/m<sup>2</sup> day, more preferably less than 2.01, and most preferably less than 1.00, are achieved. In some cases, less than 0.50 g/m<sup>2</sup> day is achieved. A second important property for preservation of food, metals, and electronics is absence or reduction of oxygen. This property can be measured by Oxygen Transition Rate (OTR) measured in cubic centimeters (cm<sup>3</sup>) of oxygen transmitted through a square meter per day at 22.8°C (73F) and 0% relative humidity. Reducing oxygen transmission can extend the life of a packaged food for people or animals. OTR's achieved by the present invention so far have been as low as 17.80, whereas the best OTR achieved by 140 gauge metallized oriented polypropylene substrates have been only 30.00.

The present invention allows lower cost materials with reduced numbers of layers needed to achieve equivalent barrier properties compared to existing packaging materials.

The following examples are presented to illustrate a few of the embodiments of the invention. In the examples, oriented polypropylene films were used as controls to monitor Moisture Vapor Transition Rates (MVTR) and Oxygen Transmission Rates (OTR). The first set of control film was left plain and is denominated as clear. The second series of control films were metallized to provide MVTR properties. In each set were films of 70 gauge and of 140 gauge.

Applications of a series of acrylate and methacrylate-terminated or internally reactive oligomer compounds were applied with a #2 wire wound rod applicator, and polymerized using a three mega-rad Electron Beam energy to polymerize the carbon-carbon double bond of the acrylates and methacrylates.

The following abbreviations are used in the examples :

PBDMA Polybutadiene Dimethacrylate Oligomer, CN 301 or CN 303 from SARTOMER

PBEA Phenyl Glycidyl Ether Acrylate Oligomer, CN 131 from SARTOMER

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	MASAHE	Maleic Anhydride Styrene Acrylate Half Ester Oligomer, like SB 400, SB 401, SB 402, SB 403, SB 404, SB 405, SB 500, SB 510, SB 520, SB 600 from SARTOMER
5	PUDA	Polyester Urethane Diacrylate Oligomer, like CN 983, CN 984, CN 985, CN 964, CN 965, CN 966, CN 962, CN 961, CN 984, CN 981, CN 982, CN 973, CN 967, CN 968 from SARTOMER
	POGUDA	Polytetramethylene Oxide Glycol Urethane Diacrylate Oligomer
10	AEA	Amino Ether Acrylate Oligomer, like CN 500, CN 501, CN 502, CN 550, CN 551, CN 371, CN 383, CN 384, CN 386, CN 388 from SARTOMER
	FAA	Fluorinated Acrylic Acrylate Oligomer
	MASAE	Maleic Anhydride Styrene Acrylate Ester Oligomer
15	PBUDA	Polybutadiene Urethane Diacrylate Oligomer, CN 302 from SARTOMER
	BAED	Bisphenol-A-Epoxy-Diacrylate Oligomer, like CN 120, CN 124, CN 104 from SARTOMER
	POUA	Polypropylene Oxide Urethane Acrylate Oligomer
20	AA	Acrylic Acrylate Oligomer + 10% Acrylic Acid
	HPA	Hydroxyl Propyl Acrylate Monofunctional Monomer (HPA from Rohms & Haas)
	HDDA	Hexanediol Diacrylate Multifunctional Monomer
25	MVTR	Moisture Vapor Transmission Rate, g/m <sup>2</sup> /day at 37.8°C (100F), 90% Relative Humidity
	OTR	Oxygen Transmission Rate, cm <sup>3</sup> /m <sup>2</sup> /day at 22.8°C (73F), 0% Relative Humidity

### EXAMPLES

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Oriented polypropylene substrates of various gauges, either metallized or clear, were coated with coating compositions comprising various oligomer compounds, which were applied to the metallized polypropylene film and polymerized with radiation.

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Moisture vapor transmission rates and oxygen transmission rates were measured for the resulting coated films. A #2 wire wound bar was



used to apply the coating compositions, which were polymerized with a three mega-rad Electron Beam dose.

This example demonstrates that application of oligomer compositions reduced the MVTR and OTR of polymeric substrates.

5 The reductions in MVTR and OTR were very significant and surprising. The free radically polymerized oligomer compositions comprised 85 parts by weight oligomer and 15 parts by weight of a multifunctional acrylate compound. The results are reported in Table 1.

10 TABLE 1

<u>Film substrate</u>	<u>Gauge</u> **	<u>Oligomer</u>	<u>Multifunctional Acrylate</u>	<u>MVTR</u>	<u>OTR</u>
* Metallized	70			3.87	30.00
Metallized	70	PBDMA	HDDA	1.89	
Metallized	70	PBEA	HPA	1.29	
Metallized	70	MASAHE	HPA	1.16	
Metallized	70	PUDA	HDDA	0.92	
Metallized	70	POGUDA	HDDA	0.63	54.50
Metallized	70	AEA	HPA	0.60	
Metallized	70	AEA	HPA	0.56	50.00
Metallized	70	FAA	HDDA	0.47	60.70
Metallized	70	FAA	HDDA	0.47	60.70
Metallized	70	MASAE	HDDA	0.46	
Metallized	70	PBUDA	HDDA	0.43	47.70
Metallized	70	PBUDA	HDDA	0.35	43.80
Metallized	70	BAED	HDDA	0.35	34.00
Metallized	70	POUA	HDDA	0.35	43.80
Metallized	70	BAED	HDDA	0.35	34.00
Metallized	70	AA	HPA	0.30	
* Clear	70			7.59	1000.00
Clear	70	AA	HDDA	0.50	
Clear	70	PBDMA	HDDA	7.40	
Clear	70	PBEA	HPA	7.16	830.30
Clear	70	POGUDA	HDDA	7.10	
Clear	70	PUDA	HDDA	6.87	193.00
Clear	70	AEA	HPA	6.70	
Clear	70	MASAE	HPA	6.37	994.90
Clear	70	AEA	HPA	6.05	
Clear	70	BAED	HDDA	5.48	137.60
Clear	70	AA	HDDA	0.50	134.30

Clear	70	POUA	HDDA	7.84	707.20
*Metallized	140			2.01	30.00
Metallized	140	PBDMA	HDDA	1.63	
Metallized	140	PUDA	HDDA	1.78	
Metallized	140	POGUDA	HDDA	1.54	
Metallized	140	AEA	HPA	1.52	
Metallized	140	AEA	HPA	1.32	
Metallized	140	FAA	HDDA	1.43	29.50
Metallized	140	MASAE	HDDA	1.54	
Metallized	140	PBDMA	HDDA	1.21	46.50
Metallized	140	BAED	HDDA	1.28	33.30
Metallized	140	PBEA	HPA	1.21	
Metallized	140	AA	HPA	1.36	
Metallized	140	AA	HDDA	1.34	23.90
Metallized	140	MASAHE	HPA	1.21	
Metallized	140	POUA	HDDA	1.08	17.80

\* indicates Comparative example

\*\* Gauge refers to the thickness of the substrate ;

100 gauge refers to 0.001 inches (25.4  $\mu$ m)

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While the invention has been described and exemplified in great detail, it should become readily apparent to those skilled in this art that various alternative embodiments can be made without departing from the spirit and scope of the invention.

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**CLAIMS**

1 - A composite material suitable for packaging moisture and/or oxygen sensitive products comprising one or more polymeric substrate(s) and one or more barrier property-providing coating(s), ink(s), and/or adhesive(s) on or between said polymeric substrate(s), said coating(s), ink(s) and/or adhesive(s) being cured from composition(s) comprising alpha, beta ethylenically unsaturated monomer(s) and/or oligomer(s), said composition(s) exclusive of amino group containing alkoxy silane compounds and vinyl alcohol resins, said composite not comprising metal foil.

2 - Composite material according to claim 1 wherein said coating(s), ink(s) and/or adhesive(s) are cured by a free radical mechanism.

3 - Composite material according to claim 1 or 2 wherein said coating(s), ink(s) and/or adhesive(s) are radiation cured.

4 - Composite material according to claim 3 wherein said radiation cured coating(s), ink(s) and/or adhesive(s) are cured by a free radical, cationic, hybrid or charge transfer mechanism.

5 - Composite material according to claim 1 wherein said unsaturated monomer(s) and/or oligomer(s) having at least one functional group selected from the group consisting of (meth)acrylate, epoxy, vinyl ether, propenyl ether, maleate and fumarate.

6 - Composite material according to claim 5 wherein said unsaturated monomer(s) and/or oligomer(s) have functionalities selected from the group consisting of (meth)acrylate, epoxy and propenyl ether.

7 - Composite material according to anyone of claims 1 to 6 having no metallized polymeric substrate.

8 - Composite material according to anyone of claims 1 to 6 having at least one metallized polymeric substrate.

9 - Composite material according to anyone of claims 1 to 8 wherein said polymeric substrate(s) are selected from the group consisting of vinylidene chloride, polyethylene, polypropylene, polyamide, cellulosic, polystyrene, poly(meth)acrylate and poly(ethylene terephthalate).

10 - Composite material according to claim 1 wherein said oligomer(s) are (meth)acrylate-functional compound(s).

11 - Composite material according to claim 10 wherein said oligomer(s) are (meth)acrylate-functional compound(s) selected from  
5 the group consisting of aliphatic polyether urethane (meth)acrylates ; aliphatic polyester urethane (meth)acrylates ; aromatic polyether urethane (meth)acrylates ; aromatic polyester urethane (meth)acrylates ; polyester (meth)acrylates ; polyether (meth)acrylates ; epoxy (meth)acrylates ; polyamine (meth)acrylates ; (meth)acrylated  
10 acrylic oligomers ; and long chain alkane (meth)acrylates.

12 - Composite material according to claim 1 wherein said composition is cured by ultraviolet (UV) or electron beam (EB) radiation.

13 - Composite material according to claim 1 wherein said  
15 polymeric substrate(s) are films, each about 10-200 microns in thickness and said composite material is comprised of at least two of said polymeric substrates films having adhesive between each film, said adhesive being radiation cured composition.

14 - Composite material according to anyone of claims 1 to  
20 13 wherein the thickness of said coating(s), ink(s) and/or adhesive(s) is about 1 to 250 microns.

15 - Composite material according to claim 14 wherein the thickness of said coating(s), ink(s) and/or adhesive(s) is about 2 to 10 microns.

25 16 - Composite material according to claim 1 comprising at least one polypropylene film substrate, at least one polyethylene terephthalate film substrate, and at least one radiation cured, barrier property-providing adhesive between said film substrates.

17 - Composite material according to claim 10 wherein said  
30 oligomer(s) are selected from the group consisting of polybutadiene dimethacrylates ; phenyl glycidyl ether acrylates ; maleic anhydride / styrene / acrylate half esters ; polyester urethane diacrylates ; polytetramethylene oxide glycol urethane diacrylates ; amino ether acrylates ; fluorinated (meth)acrylated copolymers of (meth)acrylates,  
35 (meth)acrylic acid, and fluoro(meth)acrylates ; polybutadiene urethane diacrylates ; bisphenol-A epoxy-diacrylates ; polypropylene oxide

urethane acrylates ; (meth)acrylated copolymers of (meth)acrylate / acrylic acid ; and long chain alkanediol (meth)acrylates.

18 - Composite material according to claim 10 wherein said oligomer(s) are selected from the group consisting of acrylic acrylates ; amino acrylates and epoxy (meth)acrylates.

19 - Composite material according to anyone of claims 1 to 18 wherein said composition comprising oligomer(s) further includes one or more mono-, di- or polyfunctional monomers.

20 - Article comprising a perishable material or a moisture-sensitive or oxidation-sensitive article enclosed within a package composed of a composite material according to anyone of claims 1 to 19.

21 - Article according to claim 20 wherein said package is in the form of a carton, bag or wrap.

22 - Article according to claim 20 wherein said material or article is food or an electronic component.

23 - Article according to claim 20 wherein said composite material comprises polymeric substrate(s) selected from the group consisting of polyvinylidene chloride, polyethylene, polypropylene, polyamide, cellulosic, polystyrene, poly(meth)acrylate and poly(ethylene terephthalate), said radiation-cured oligomer(s) are selected from aliphatic polyether urethane (meth)acrylates ; aliphatic polyester urethane (meth)acrylates ; aromatic polyether urethane (meth)acrylates ; aromatic polyester urethane (meth)acrylates ; polyester (meth)acrylates ; polyether (meth)acrylates ; epoxy (meth)acrylates ; polyamine (meth)acrylates; (meth)acrylated (meth)acrylic oligomers ; and long chain alkane (meth)acrylates and said coating(s), adhesive(s) and/or ink(s) are cured with EB or UV radiation.

24 - Method of improving the barrier properties of polymeric substrates comprising applying a barrier property-providing amount of a coating, ink or adhesive on said substrate, or between two or more of said substrates, said coating, ink or adhesive comprising an oligomeric compound and curing by means of free radical polymerization.

25 - Method according to claim 24 wherein said curing is obtained by subjecting the oligomeric compound to sufficient radiation to cure said compound.

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26 - Method according to claim 24 wherein said polymeric substrates are selected from the group consisting of metallized or non-metallized polyvinylidene chloride, polyethylene, polypropylene, polyamide, cellulosic, polystyrene, poly(meth)acrylate, and poly(ethylene terephthalate) ; said oligomer is selected from the group consisting of aliphatic polyether urethane (meth)acrylates ; aliphatic polyester urethane (meth)acrylates ; aromatic polyether urethane (meth)acrylates ; aromatic polyester urethane (meth)acrylates ; polyester (meth)acrylates ; polyether (meth)acrylates ; epoxy (meth)acrylates ; polyamine (meth)acrylates ; and (meth)acrylated acrylic oligomers and fluorinated (meth)acrylated acrylic oligomer ; and said oligomer is cured by radiation.

# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 99/10070

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B32B27/30 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 344 589 A (BASF AG) 6 December 1989 (1989-12-06) page 2, line 44-52 page 5, line 29-39 page 5, line 58 -page 6, line 4; claims 1,3	1-9,23
X	WO 98 18852 A (CATALINA COATINGS INC ;DAWSON ERIC P (US); LANGLOIS MARC (US); CLI) 7 May 1998 (1998-05-07) page 5, line 8-30 page 6, line 28 -page 7, line 3 page 15, line 17 -page 17, line 10	1-26
X	EP 0 374 632 A (WOLFF WALSRÖDE AG) 27 June 1990 (1990-06-27) claims 1,2	1-9

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Von Kuzenko, M

# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 360 385 A (ICI PLC) 28 March 1990 (1990-03-28) page 2, line 6-9; example 1 ---	1-9
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 110 (C-109), 22 June 1982 (1982-06-22) & JP 57 038828 A (YOSHINO KOGYOSHO CO LTD), 3 March 1982 (1982-03-03) cited in the application abstract ---	1-9
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 245 (M-418), 2 October 1985 (1985-10-02) & JP 60 097823 A (MITSUI TOATSU KAGAKU KK), 31 May 1985 (1985-05-31) abstract -----	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Appl. No.

PCT/EP 99/10070

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0344589 A	06-12-1989	DE 3818425 A AT 78850 T JP 2028278 A	07-12-1989 15-08-1992 30-01-1990
WO 9818852 A	07-05-1998	AU 5100298 A CN 1238792 A EP 0935633 A	22-05-1998 15-12-1999 18-08-1999
EP 0374632 A	27-06-1990	DE 3842948 A BR 8906600 A CA 2005968 A DD 290368 A DK 649989 A JP 2225043 A MX 171491 B NO 174769 B US 5126198 A	28-06-1990 04-09-1990 21-06-1990 29-05-1991 22-06-1990 07-09-1990 29-10-1993 28-03-1994 30-06-1992
EP 0360385 A	28-03-1990	BR 8903663 A CN 1039758 A, B JP 2074336 A US 5089347 A	13-03-1990 21-02-1990 14-03-1990 18-02-1992
JP 57038828 A	03-03-1982	NONE	
JP 60097823 A	31-05-1985	NONE	

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